

# Flameless incineration of pyrene under sub-critical and supercritical water conditions\*

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## Abstract

Pyrene was used as a typical four-ring polycyclic aromatic hydrocarbon (PAH), to investigate the mechanisms and incineration behaviour of large organic molecules in a batch supercritical water oxidation reactor using hydrogen peroxide as oxidant. The distribution of carbon as gaseous species and organic species in relation to the temperature and pressure, and reaction time was monitored. The results showed that at 200 °C, pyrene was only slightly decomposed but as the temperature increased to 250 °C and then to 280 °C, carbonisation and thermal cracking became prevalent leading to char formation and decomposition of pyrene to phenanthrene, and later naphthalene. Rapid dissolution and oxidation of the char and organic species started occurring from 300 °C. Increasing reaction time resulted in increased formation of carbon dioxide and carbon monoxide. Initially high product formation of phenanthrene at short reaction times was followed by high decomposition of the organic products in solution as the reaction conditions became progressively more severe. Oxygenated organic species such as aldehydes, ketones, phenols, xanthone, and benzoic acid were identified as the temperature and reaction times were increased between 300 and 380 °C. From the analytical results obtained, carbon mass balances were calculated for each experiment. A proposed mechanism for the observed oxidative decomposition of pyrene is also reported.

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**Keywords:** Incineration; Sub-critical; Supercritical water oxidation; PAH; Pyrene

## 1. Introduction

Flameless incineration of organic compounds at conditions of the supercritical region of water is being developed as a thermochemical treatment method for wastes that are rich in organic compounds and residues such as sewage sludge, sludge from waste treatment plants, military wastes and a variety of industrial wastes. The process involves the oxidative decomposition of target organic molecules in an aqueous medium to mainly carbon dioxide and water, in the presence of oxygen or oxygen source. Supercritical water ( $T_C \geq 374$  °C,  $P_C \geq 22.1$  MPa) oxidation has been regarded as a flameless combustion process since the reaction rates are comparable with combustion although the process is flameless [1]. The process is being developed as an alternative to incineration

of aqueous wastes containing low to moderate concentrations of organic materials, and as a potential process for limiting the problems of secondary pollution arising from alternative waste treatment processes [2]. It is well known now that sub-critical and supercritical water behave in a similar manner to common organic solvents having high thermal stability [3]. A variety of chemical reactions including bond fission, rearrangement, hydration and dehydration, hydrolysis, partial and complete oxidation in supercritical water have been reported [4,5].

Many supercritical water oxidation (SCWO) experiments have been conducted at temperatures above 600 °C and pressures from 25 MPa, requiring extreme engineering and materials standards using mainly oxygen and air [6,7]. In supercritical water, organic compounds become soluble and gases are completely miscible, so that in the presence of an oxidant like oxygen gas, organic compounds are converted mainly to carbon dioxide and water. Hydrogen peroxide has proven to be an alternative oxidant to air or pure oxygen [8–11]. Comparably high destruction efficiencies (up to 99.999%) have been achieved at lower temperatures of 400 °C at a residence time of 30 min,

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using hydrogen peroxide as the oxidant in a batch reactor [8]. The initiation of reactions by the hydroxyl radical is expected to be much faster as compared to that by oxygen in typical wet oxidation conditions [8]. Hydrogen peroxide decomposes to form hydroxyl radicals, and later oxygen gas [12]. Hence, it would appear that subsequent oxidation of intermediate hydroxylated species would occur much more rapidly as the hydrogen peroxide decomposes to oxygen and water.

Large tonnages of organic and inorganic chemicals are released annually into the environment from various anthropogenic sources including oil and chemical spillages, industrial effluents, agricultural and sewage storm waters, etc. Polycyclic aromatic hydrocarbons (PAH) are a group of ubiquitous chemicals that occur widely in the environment. Their widespread distribution may be due to their chemical inertness, making them the possible stable end-products of the degradation of biochemicals in the environment. Polycyclic aromatic hydrocarbons exhibit very poor solubility in water at ambient conditions. The highest water solubility of any pure PAH is that of naphthalene, which is 0.317 ppm at 25 °C; however, where they occur in industrial wastewaters and sewage storm water, the presence of organic solvents can enhance their apparent solubility due to micelle formation [13]. They have been shown to be resistant to thermal decomposition under supercritical water conditions for up to 6 h, only decomposing by a few parts per million [4]. However, the decomposition of some three- to six-ringed PAHs in supercritical water oxidation conditions has been reported to reach up to 99% [9]. Moreover, these compounds have been studied for a long time as a possible risk to human health [9]. Some PAHs such as benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene and benzo[a]anthracene have been confirmed as carcinogens and mutagens [14].

Knowledge of the basic chemistry of the processes occurring within the reactor is needed for suitable application of the SCWO process. Excellent destruction efficiencies measured in terms of the parameters of gross organic pollutants such as chemical oxygen demand and total organic carbon are seen in the literature. While these reports confirm the effectiveness of SCWO in the decomposition of organic pollutants, there is further need to monitor the thermochemical processes in terms of detailed analyses of target model compounds, intermediates and possible final products to understand and therefore optimise the process conditions. This paper presents an investigation of the processes occurring during the oxidation of a polycyclic aromatic hydrocarbon namely pyrene, in water (density, 0.2 g/ml) from 200 to 380 °C in a batch (autoclave) reactor, using hydrogen peroxide as the oxidant. Pyrene is a typical thermally stable PAH with poor solubility in water (ca. 130 µg/l), making it easily recoverable from an aqueous medium. Its size and structure also give the possibility of producing intermediate reaction products that can easily be monitored during the experiments.

## 2. Materials and methods

### 2.1. Reactor assembly and reagents

The reactor (Fig. 1) was obtained from the Parr Instrument Co. USA, and was made of stainless steel (SS 316) with a volume capacity of 500 ml designed to a maximum temperature and pressure of 500 °C and 35 MPa, respectively. The reactor was heated by a 3 kW ceramic heater obtained from Elmatic (Cardiff) Limited, UK. Pyrene of 99% purity and other analytical reagents were obtained

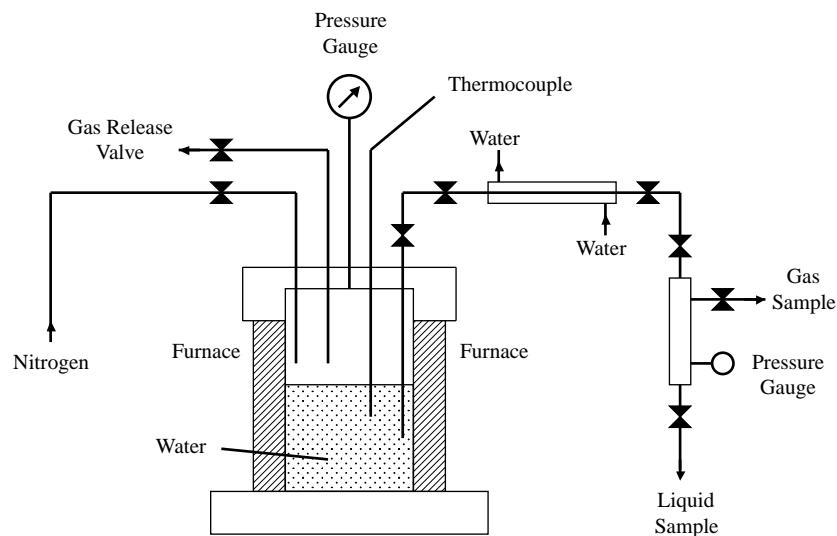


Fig. 1. Schematic diagram of the reactor assembly.

from Sigma Aldrich, UK. Hydrogen peroxide (30% w/v) obtained from Supelco, UK was used as the oxidant throughout the experiments.

## 2.2. Procedure

The pyrene (0.1 g) was weighed out into the reactor, a known volume of water added, followed by a known volume of hydrogen peroxide to bring the total volume of liquid to 100 ml. Nitrogen gas was used to purge the reactor for 10 min. After purging, the reactor was heated at 7.5 °C/min. Two sets of experiments were conducted to monitor the effect of reaction time and temperature on the decomposition of pyrene. In the first set of experiments, as soon as a set temperature was reached, the reactor was held for a specified time, e.g. 0, 30, 60, or 120 min. In the second set of experiments, where the effect of temperature was monitored, the heating was stopped at the designated temperatures of 200, 250, 280, 300, 350, 370, and 380 °C. At the end of each experiment, the reactor was removed from the heater and placed in a cold water jacket to rapidly quench the reaction. The final temperature and pressure were noted just before sampling.

## 2.3. Gas sampling and analysis

The gaseous effluent was sampled via a gas/liquid sampling system and immediately analysed on a Varian CP-3380 gas chromatograph with a thermal conductivity detector (GC/TCD) for hydrogen, oxygen, carbon dioxide, carbon monoxide, methane, and nitrogen. The column used was a 2 m length by 2 mm diameter column, packed with 60–80 mesh molecular sieve. Argon was used as the carrier gas. The column oven was held isothermally at 30 °C for the analysis; the injector oven was at 120 °C. The detector oven operated at 120 °C with filament temperature of 160 °C. The instrument comprised of two columns; one was used to separate hydrogen, oxygen, nitrogen, methane, and carbon monoxide, while the other was used for the analysis of carbon dioxide. The injectors were fitted with a self-sealing silicon rubber septum. Hydrocarbons from C<sub>1</sub> to C<sub>4</sub> were analysed using a second Varian CP-3380 gas chromatograph with a Flame Ionisation Detector (GC/FID). The column used was 2 m long with 2 mm diameter packed with 80–100 mesh Hysesp. Nitrogen was used as the carrier gas. The temperature was programmed to start at 60 °C for 3 min, ramped at 10 °C/min to 100 °C, held for 3 min, finally ramped to 120 °C at 20 °C/min and held for 9 min. The injector fitted with a self-sealing silicon rubber was held at 150 °C while the detector temperature was 200 °C.

## 2.4. Liquid effluent sampling and analysis

Pyrene and other reaction products in the derived liquid were analysed using liquid column chromatography

fractionation followed by gas chromatography. The reactor was opened to sample its total liquid content. The reactor was washed 2–3 times with known aliquots of acetone and the washes added together with the liquid effluent. After mixing, the acetone was discharged with a gentle stream of nitrogen gas for 10 min, after which the effluent was filtered. The sample was extracted largely using the solid phase extraction protocol reported by Kootstra et al. [15]. The sorbent was DSC-18 (C-18) obtained from Supelco, UK. 500 mg of the sorbent was loaded into a 10 ml glass reaction tube and rinsed twice with dichloromethane (DCM) and then conditioned using methanol, and deionised water at a constant flow rate. The liquid effluent sample was eluted on the column at the same rate after which the column was dried under vacuum for a specific period of time. The organic compounds were extracted using two aliquots of dichloromethane. The first aliquot of the DCM was used to soak the sorbent for 5 min before eluting with the second. After eluting, the eluate was either re-concentrated by using a gentle stream of nitrogen gas or diluted with known amounts of DCM to a constant volume. The prepared samples were injected directly into a Fisons 8000 series gas chromatography with a flame ionisation detector (GC/FID). The column was a non-polar polydimethylsiloxane DB-5 capillary column 30 m by 0.32 mm with on-column injection. The temperature programme was 40–100 °C at 15 °C/min heating rate, held at 100 °C for 1 min followed by heating to 260 °C at 4 °C/min heating rate and held at 260 °C for 10 min. Identification of compounds was also aided by coupled gas chromatography/mass spectrometry (GC/MS) with auto-injection. The system used was a Hewlett Packard 5280 gas chromatograph fitted with a Restek RTX-5ms column, coupled to a HP5271 ion trap detector. The ion mass spectra derived were automatically compared to spectral libraries using HP Chemstation software and species were judged to be reliably identified when spectra match was greater with 70. The same temperature programme as used in the GC/FID was adopted for the GC/MS. Both gas chromatographs used helium as carrier gas.

The repeatability of the experimental system was tested with thorough analysis of the gas sampling repeatability, the response factor repeatability on the gas chromatograph, component analysis repeatability in the derived reaction solution and overall experimental repeatability. Examples of the reproducibility of the analyses of components of the effluent gases during the oxidation of pyrene are shown in Table 1. The errors in carbon dioxide and oxygen, the main gases were small. However, the error in carbon monoxide and especially hydrogen were higher because of the relatively small percentages of these gases in the effluent gases. The contribution of hydrogen product gas to mass balances was negligible. The overall experimental repeatability was very good.

Table 1

Reproducibility of components of effluent gases obtained during hydrothermal oxidation of pyrene in relation to reaction temperature

Repeat experiment no.	CO <sub>2</sub>	CO	Hydrogen	Oxygen
<i>Oxidation at 300 °C</i>				
1	1.59	0.09	0.02	98.3
2	1.67	0.10	0.03	98.2
3	1.57	0.10	0.03	98.3
Mean	1.61	0.10	0.03	98.3
Standard deviation	0.05	0.01	0.01	0.06
Rel. standard deviation (%)	3.18	5.97	21.7	0.06
<i>Oxidation at 350 °C</i>				
1	3.45	0.28	0.07	96.2
2	3.50	0.33	0.07	96.1
3	3.30	0.32	0.08	96.3
Mean	3.42	0.31	0.07	96.2
Standard deviation	0.10	0.03	0.01	0.10
Rel. standard deviation (%)	3.05	8.53	7.87	0.10
<i>Oxidation at 380 °C</i>				
1	6.9	0.33	0.07	92.7
2	7.2	0.32	0.08	92.4
3	7	0.31	0.09	92.6
Mean	7.03	0.32	0.08	92.6
Standard deviation	0.15	0.01	0.01	0.15
Rel. standard deviation (%)	2.17	3.13	12.5	0.17

### 3. Results and discussion

#### 3.1. Effect of temperature

**Table 2** shows the product yield from the sub-critical and supercritical water oxidation of pyrene in relation to the effect of temperature from 200 to 380 °C. The main gases produced were carbon dioxide and carbon monoxide. As the pyrene became increasingly oxidised as the temperature and therefore pressure of the system was increased, increasing amounts of carbon dioxide and carbon monoxide were

produced. Correspondingly, there was a decrease in the concentration of pyrene. The formation products from the decomposition of pyrene in the liquid phase were mainly phenanthrene and naphthalene, which showed an increase followed by a decrease as the oxidation conditions became more severe. Similarly, there was initial char formation at lower temperatures followed by oxidation of the char as the temperature of reaction increased to reach eventually at 380 °C, supercritical water oxidation conditions. Water is a known reaction product from the sub-critical and supercritical water oxidation of organic compounds, however, since the reactions were carried out in a large excess of water, the product water yield was not measured.

**Table 3** shows the distribution of carbon as gas (mainly carbon dioxide and carbon monoxide), as char and as organic compounds during the oxidative decomposition of pyrene as a function of temperature from 200 to 380 °C. The mass of carbon in any carbon containing species was calculated from the mass of the carbon containing species identified, the molecular formula of the species and the molecular mass of the carbon containing species. The concentrations of the gases were obtained in mole percent from the gas chromatograph. The partial pressure of each individual gas was calculated and was used to calculate the number of moles of the gases formed from the general gas equation. The oxidant was 6% hydrogen peroxide, which was more than 1000% of the stoichiometric amount required for the complete oxidation of 0.1 g of pyrene to carbon dioxide and water. At lower temperatures of 200–280 °C significant amounts of char were formed but these were oxidized to CO<sub>2</sub>, etc. as the temperature increased. At this stage, the liquid effluent after reaction was reddish-brown to black in colour. The formation of char may have resulted from thermal cracking of pyrene at the walls of the reactor since there was no stirring taking place. The insolubility of pyrene in ambient water did not seem to be responsible for the thermal cracking process, since soluble phenol also showed similar characteristics under similar conditions. This same process was responsible for the thermal breakdown of pyrene to phenanthrene and subsequently naphthalene and other alkenes and alkanes [16] from 250–280 °C. Neither phenanthrene nor naphthalene was found at 200 °C. The concentration of phenanthrene increased with temperature to 280 °C but started decreasing due to oxidation by

Table 2

Product yield from the oxidation of pyrene in relation to temperature

Temperature	CO <sub>2</sub> (mol%)	CO (mol%)	Pyrene (wt%)	Phenanthrene (wt%)	Naphthalene etc (wt%)	Char (wt%)
200	0.4	0.00	91.3	0.0	0.0	1.3
250	0.6	0.00	86.1	8.7	0.0	3.6
280	1.1	0.006	69.6	14.3	0.0	3.3
300	1.6	0.094	54.2	12.2	11.6	0.1
350	3.4	0.280	33.6	9.6	9.9	0.0
370	5.4	0.300	18.8	4.9	6.8	0.0
380	6.9	0.300	5.5	0.1	2.3	0.0

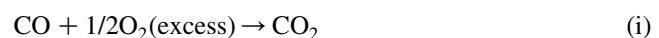
oxygen produced from the decomposition of hydrogen peroxide. At 300 °C, the liquid effluent had become brownish and was almost pure colourless water at 380 °C indicating near complete oxidation under supercritical conditions.

Table 3 shows that, in general, the percentage by mass of the carbon-bearing species with respect to the mass of the starting material was close to, but did not total 100%. Some of the carbon dioxide formed may have dissolved in water forming carbonic acid, however, no attempt was made to analyse this. In all experiments, some amounts of pyrene, phenanthrene, and naphthalene were always found at each stage of the reaction, however, these reached significantly lower levels as the temperature and reaction time was increased. As the temperature increased, the levels of phenanthrene generally decreased but in most experiments, naphthalene either increased or remained as a final product. No dimers or polymeric compounds were detected in these oxidation experiments in contrast to those reported in pyrolytic and ordinary decomposition experiments in the absence of oxygen or oxygen source [3,16].

The composition of the product gas collected from the experiments between the reaction temperatures of 200 and 280 °C showed only the presence of carbon dioxide, and large amounts of oxygen from the hydrogen peroxide. No carbon monoxide or hydrogen was found. Small amounts of methane (<0.01%) were detected at these reaction conditions. The carbon dioxide may have been formed from the oxidation of the alkenes and alkanes, including methane, formed during the thermal cracking of pyrene [17]. The reactor pressure and molar volume of water increased with increase in temperature. The increase of the molar volume around the near critical region caused rapid dissolution [18] and oxidation of the formed char. The gaseous products found were mainly carbon dioxide and small amounts of carbon monoxide and hydrogen. In addition, oxygen was produced from the decomposition of hydrogen peroxide. Methane was found only when the amount of hydrogen peroxide was less than 6% even up to 380 °C. This confirmed that a large excess of oxygen was required for complete oxidation [11].

Carbon monoxide may have been formed from the decarbonylation of some intermediate carbonyl compounds formed during the oxidation of organic species at lower

temperatures and hence lower water density in the reactor [16]. There was a general increase in the level of CO with time within each isothermal set of experiments. More CO was found at lower temperatures than at higher temperatures. However, the concentration of carbon monoxide remained very low throughout the experiments. There were three possible reaction routes that could consume the carbon monoxide formed; these were oxidation by excess oxygen to carbon dioxide (i), water–gas shift (ii), and methanation (iii)



However, since methane was rarely found, the high density of water at near the critical point must have suppressed the methanation route; this phenomenon also inhibits decarbonylation so that less CO is formed in the first place [16]. A small amount of hydrogen was formed possibly as a result of the water–gas shift and combination of free hydrogen radicals. The survival of carbon monoxide even in the presence of large oxygen concentration could be explained by the reverse water–gas shift due to larger concentration of carbon dioxide and held in equilibrium at high temperature and pressure by large concentration of water in a closed system consisting of a single fluid phase around and up to the supercritical conditions. Generally, there was a positive correlation between the level of hydrogen and carbon monoxide found.

### 3.2. Effect of reaction time

The influence of reaction time was investigated by holding the reactor isothermally and adiabatically for a specified time of up to 120 min. The temperature range considered was 300–380 °C. The results are reported in Table 4 for the product yield and Table 5 for the carbon distribution. Within each set of isothermal experiments, the rates of pyrene conversion appeared to be more rapid during the first 30 min of reaction and slowed down afterwards. The initiating faster conversions of organic compounds in sub-critical and supercritical water oxidation conditions have been reported [8,19].

Table 3  
Carbon distribution in products from the oxidation of pyrene in relation to temperature

Temperature	CO <sub>2</sub> carbon (%)	CO carbon (%)	Pyrene carbon (%)	Phenanthrene carbon (%)	Naphthalene, etc. carbon (%)	Char carbon (%)
200	3.9	0.0	86.8	0.0	0.0	1.3
250	6.0	0.0	81.8	8.2	0.0	3.6
280	10.8	0.0	66.2	13.5	0.0	3.3
300	18.9	1.1	51.5	11.5	10.9	0.1
350	40.2	3.3	31.9	9.1	9.3	0.0
370	63.8	3.5	17.9	4.6	6.4	0.0
380	81.6	3.5	5.2	0.1	2.2	0.0

Table 4

Product yield from the oxidation of pyrene in relation to reaction time

Reaction time (min)	CO <sub>2</sub> (mol%)	CO (mol%)	Pyrene (wt%)	Phenanthrene (wt%)	Naphthalene, etc. (wt%)
<i>300 °C–95 bar</i>					
0	1.6	0.09	54.2	12.2	11.6
30	4.1	0.34	30.3	6.7	7.1
60	5.4	0.38	18.9	6.1	3.4
120	5.6	0.55	16.9	1.0	2.9
<i>350 °C–170 bar</i>					
0	3.4	0.28	33.6	9.6	9.8
30	5.9	0.31	17.8	7.4	2.0
60	5.8	0.46	17.3	4.5	1.1
120	6.1	0.48	10.9	3.4	1.4
<i>370 °C–205 bar</i>					
0	5.4	0.30	18.8	4.9	6.8
30	6.1	0.37	12.5	3.0	0.9
60	6.5	0.39	11.3	3.1	0.9
120	6.8	0.41	6.9	1.1	0.5
<i>380 °C–225 bar</i>					
0	6.9	0.30	5.5	0.1	2.3
30	7.3	0.31	2.7	0.0	0.5
60	7.7	0.32	3.4	0.0	0.1
120	7.6	0.35	1.7	0.0	0.3

The colour of the liquid effluent changed from brownish to light yellow as the reaction proceeded from 0 to 120 min at 300 °C. Analysis of the liquid effluents obtained from those runs in which the reactor was held for increasing reaction time showed that many oxygenated aromatic and aliphatic organic species were being formed in addition to the surviving pyrene, phenanthrene, and naphthalene. Some of the species found were xanthone, hydroxypyrenes, phenanthrenequinone, anthracenequinone, phenol, benzaldehyde, and benzoic acid. Fig. 2 shows an example of the reaction products found for the oxidation of pyrene at

350 °C and reaction time of 0 min. Their highest concentrations, especially for benzoic acid were found at 300 °C after reacting for 120 min. Kronholm et al. [9] found benzaldehyde, phenol, benzoic acid, quinoline, biphenyl, dibenzofuran, fluorenone xanthone, and anthracenequinone during the pressurized hot water extraction and subsequent oxidation of different PAHs at 300 °C. Our experiments showed that dibenzofuran and fluorenone were mainly reaction intermediates of biphenyl and fluorene, respectively (not shown). Some of the aliphatic compounds found were butanol, acetaldehyde, acetic acid and 2-butanone.

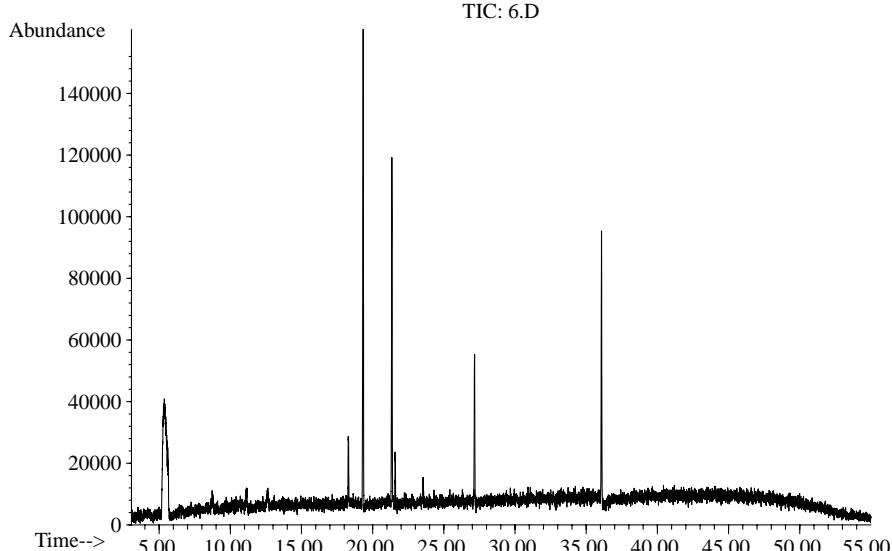


Fig. 2. Typical total ion chromatogram of the GC/MS analysis of the reaction products from the supercritical water oxidation of pyrene (350 °C, 0 min reaction time). (Phenol + naphthalene + benzaldehyde + benzoic acid, RT = 5.04 min; 9H-Fluorenone; RT = 18.2 min; phenanthrene, RT = 19.4 min; xanthone, RT = 22.8 min; hydroxyfluorenone, RT = 22.9 min; pyrene, RT = 27 min; dimethyl phthalate (standard), RT = 36 min).

The persistence of C<sub>4</sub> compounds could be an indication of the type of alkenes and alkanes formed at the earlier stages of the process [16].

No aliphatic compounds were identified in the liquid effluents from 350 to 380 °C, not because they were not formed but probably because they were quickly converted to carbon dioxide on formation under high temperature and pressure and large excess of oxygen [19].

Table 5 shows the distribution of carbon as gas and as organic compounds in relation to reaction time at various temperatures. During the experiments at 350 °C, the gasification of pyrene to carbon dioxide reached 40% at 0 min but increased to 72% after 2 h. The oxygenated aromatic compounds in the liquid phase, persisted at slightly higher levels at 350 °C up to 60 min. At this stage more benzoic acid had been formed possibly from the oxidation of benzaldehyde. Also some fluorenone was found. After reacting for 120 min the oxygenated aromatics found were benzaldehyde, benzoic acid, and xanthone.

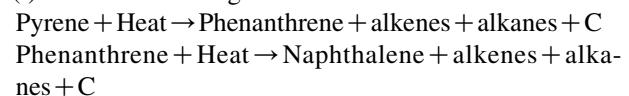
At 370 and 380 °C reaction temperature, all the other oxygenated aromatics except xanthone and benzoic acid were only found for up to 60 min. The xanthone disappeared after reaction at 370 °C for 120 min. Benzoic acid remained the only oxygenated compound found at 380 °C even after 120 min. Benzoic acid is known to be refractory and a product of decomposition of polycyclic aromatic compounds in supercritical water [9,16]. Conversion of pyrene to carbon dioxide was higher than 70% in 0 minutes, and reached 90% after 120 min. Apart from the reaction temperatures between 250 and 280 °C, significant concentrations of phenanthrene were also found during the reactions at 370 °C. Fang and Kozinski [19] reported this reappearance of phenanthrene during the decomposition of

benzo[a]pyrene near the supercritical region and they attributed it to intensive oxidative decomposition of benzo[a]pyrene. At 380 °C, even at 0 min, over 90% of the pyrene had been converted and at 30 min and above, the percentage oxidation reached 98%.

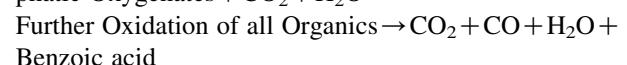
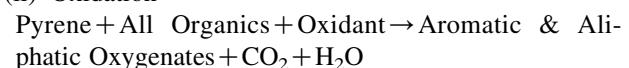
### 3.3. Proposed reaction scheme

The results of the experiments in relation to reaction temperature showed that two main processes took place. Initially, the prevailing thermochemical processes were thermal cracking and carbonisation of pyrene on the walls of the reactor at lower temperatures. However, as the temperature and corresponding pressure increased to around the near-critical conditions, the prevailing chemical processes were dissolution and oxidation [9,16,19].

#### (i) Thermal cracking and carbonisation



#### (ii) Oxidation



The oxidation of organic compounds in supercritical water takes place at intrinsically high reaction rates, sometimes in milliseconds. Hence, it was difficult to find large concentrations of intermediate compounds at any point in time, however, using the compounds identified, a reaction scheme can be proposed (Fig. 3). The pyrene was

Table 5  
Carbon distribution in products from the oxidation of pyrene in relation to reaction time

Reaction time (min)	CO <sub>2</sub> carbon (%)	CO carbon (%)	Pyrene carbon (%)	Phenanthrene carbon (%)	Naphthalene, etc. (%)
<i>300 °C–95 bar</i>					
0	18.9	1.1	51.5	11.5	10.9
30	48.5	4.0	28.8	6.3	6.8
60	63.8	4.5	18.0	5.8	3.2
120	66.2	6.5	16.1	0.9	2.8
<i>350 °C–170 bar</i>					
0	40.2	3.3	31.9	9.1	9.3
30	69.8	3.7	16.9	7.0	1.9
60	68.6	5.4	16.4	4.3	1.0
120	72.6	5.8	10.4	3.2	1.3
<i>370 °C–205 bar</i>					
0	63.8	3.5	17.9	4.6	6.4
30	72.1	4.4	11.9	2.8	0.8
60	75.6	4.6	10.7	2.9	0.8
120	80.4	4.8	6.6	1.0	0.5
<i>380 °C–225 bar</i>					
0	81.6	3.5	5.2	0.1	2.2
30	86.3	3.7	2.6	0.0	0.5
60	88.9	3.7	3.2	0.0	0.1
120	88.3	4.1	1.6	0.0	0.3

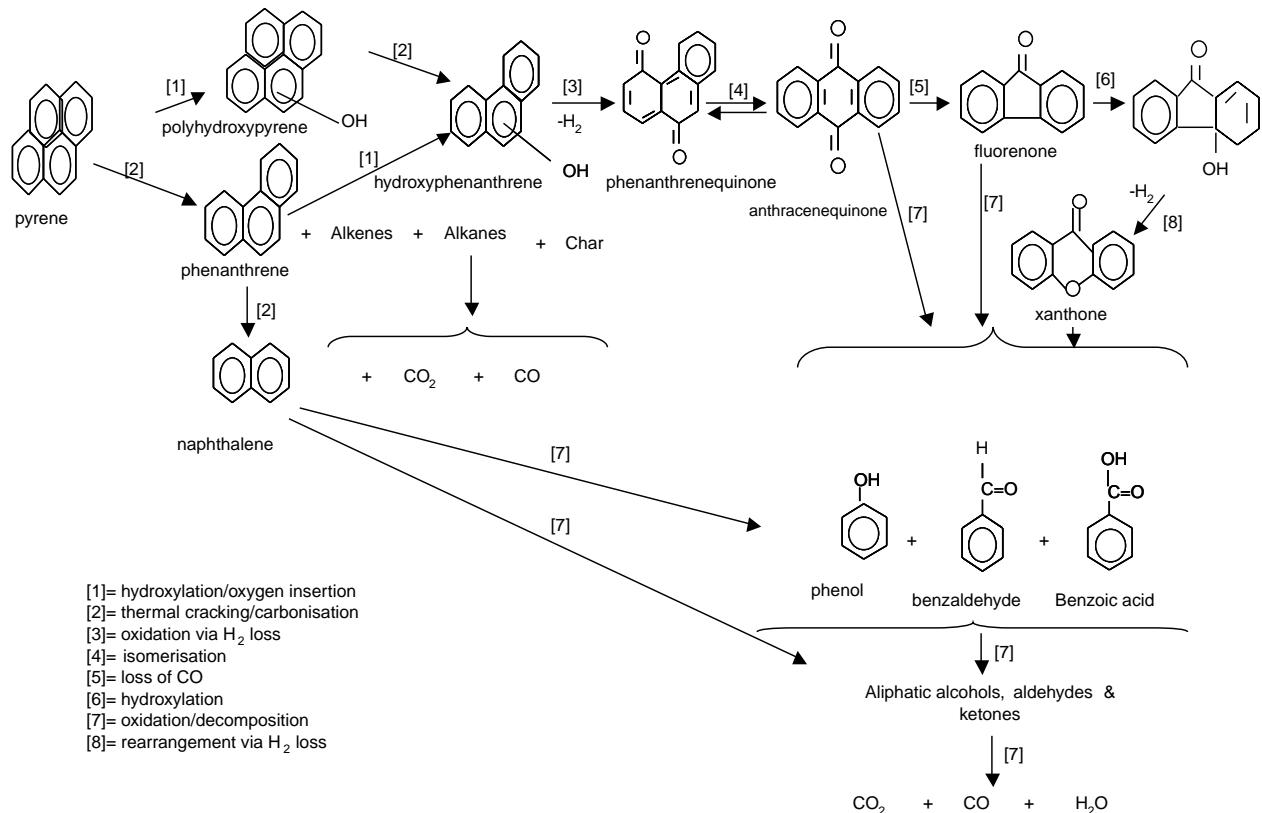


Fig. 3. Proposed reaction mechanism for the oxidative decomposition of pyrene in water.

thermally cracked or hydroxylated by hydrogen peroxide before cracking. The main product of these processes was phenanthrene and some alkenes, alkanes, and char. The lower hydrocarbons and char would be easily decomposed to carbon dioxide and water [19]. The phenanthrene and/or hydroxyl phenanthrene would be oxidized to carbonyl compounds such as ketones such as quinones, xanthone, and fluorenone, which were identified in the effluent. These compounds would then undergo chemolysis initiated by OH and oxygen radicals under supercritical water conditions to form phenols, benzaldehyde and benzoic acid. From these compounds aliphatic acids, ketones and aldehydes would form, which would then be further oxidized to carbon dioxide and water. There was sufficient evidence to suggest that the effect of hydrogen peroxide as oxidant went beyond oxidation. Using 3% hydrogen peroxide, which was more than 500% of the stoichiometric requirement for complete oxidation of 0.1 g of pyrene, produced up to 40% excess oxygen in the effluent gas but gave less than 70% pyrene conversion for a reaction time up to 1 h at 380 °C.

#### 4. Conclusions

The decomposition of pyrene, a four-ring polycyclic aromatic hydrocarbon has been investigated under subcritical and supercritical water oxidation conditions. The results showed that at 200 °C, pyrene was only

slightly decomposed but as the temperature increased to 250 and then 280 °C, carbonisation and thermal cracking became prevalent leading to char formation and decomposition of pyrene to phenanthrene, and later naphthalene. Rapid dissolution and oxidation of the char and organic species started occurring from 300 °C. Increasing reaction time resulted in an increased formation of carbon dioxide and carbon monoxide. Initially high product formation of phenanthrene at short reaction times was followed by high decomposition of the organic products in solution as the reaction conditions became progressively more severe. A number of oxygenated organic species including aldehydes, ketones, phenols, xanthone, and benzoic acid were identified. From the analytical results obtained, carbon mass balances were calculated for each experiment. The proposed mechanism for the observed oxidative decomposition of pyrene suggest that the main reaction product was phenanthrene and some alkenes, alkanes, and char. The lower hydrocarbons and char easily decompose to carbon dioxide and water. The phenanthrene and/or hydroxyl phenanthrene would be oxidized to carbonyl compounds such as ketones such as quinones, xanthone and fluorenone, which were identified in the effluent. These compounds would then undergo chemolysis initiated by OH and oxygen radicals under supercritical water conditions to form phenols, benzaldehyde, and benzoic acid.

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